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Change of a Flexible Polymer's Free Energy Due to Excluded Volume, Molecular Architecture and the Presence of Boundaries

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ABSTRACT: The free energy of an isolated polymer is a particularly sensitive function of the small-scale details of the polymer, so that a universal description of the free energy would, at first, seem unlikely. However, numerical data are used to show that the change in free energy ΔF between self-avoiding and unrestricted random walks is a nearly universal ("quasi-universal") function of the dimensionality. Starting from this observation we then apply the two-parameter model with a cutoff in conjunction with the renormalization group method to calculate ΔF for Gaussian chains perturbed by repulsive excluded-volume interactions. The additional effects of chain architecture (whether the polymer is linear, ring-shaped, or starlike) and the effects of surface proximity are also considered. Comparison of ΔF obtained from lattice chain data in the limit of long chains and ΔF obtained from our model calculations produces reasonable agreement for a number of two- and three-dimensional lattices.

1. Introduction

The two-parameter (TP) model of excluded volume in conjunction with the renormalization group (RG) method has been very successful in describing a number of large-length scale polymer properties such as the radius of gyration R_G, the second virial coefficient A_2, etc.[1,2] These properties may be adequately discussed in terms of a few coarse-grained phenomenological parameters that characterize the collective influence of the underlying microscopic interactions. In contrast, properties that show a sensitive dependence on details of the lattice or interaction potential are not expected to be well described by the two-parameter continuum model.[2]

The free energy of a lattice polymer is one property that depends very strongly on the coordination number of the lattice and on the long- and short-range interactions between chain segments. At first sight, it would, therefore, appear that the free energy does not have a universal description. On the other hand, some of the few *exact* results[3] for self-avoiding walks involve the universal scaling behavior of the number of polymer configurations C_n, which is related to the free energy, and it is of interest to compare these results with approximate analytical theories.

The self-avoiding walk limit C_n(SAW) obeys the well-known relation of Hammersley[3]

$$C_n(\mathrm{SAW}) \sim \mu^n, \qquad n \to \infty \tag{1.1a}$$

where n is the number of steps in the walk and μ is the "effective coordination number" or "connectivity constant" of the self-avoiding walk. (The symbol μ is often used in expressions like (1.1a) to describe the connectivity constant of many different kinds of walks, but here it refers *solely* to the self-avoiding limit.) Lattice simulations[4] indicate that limiting subdominant corrections to (1.1a) are of the form

$$C_n(\mathrm{SAW}) \sim \mu^n n^{\gamma-1} \tag{1.1b}$$

where γ is an exponent that depends only on the dimension of space. Similarly, the number of configurations of an unrestricted random walk C_n(RW) is given by[5a]

$$C_n(\mathrm{RW}) = q^n \tag{1.2}$$

where q is the lattice coordination number with $\mu \leq q - 1$. The definition of the configurational free energy $-F/k_BT = \ln C_n$, with k_BT the thermal energy unit, implies that the free energy difference $\Delta F = F(\mathrm{SAW}) - F(\mathrm{RW})$ is given by

$$-\Delta F/k_BT = \ln\,[C_n(\mathrm{SAW})/C_n(\mathrm{RW})] \tag{1.3a}$$

Using (1.1) and (1.2) in the limit of long chains converts ΔF to

$$-\Delta F/k_BT \sim \ln\,(\mu/q)^n, \qquad n \to \infty \tag{1.3b}$$

Data presented in section 2 demonstrate that ΔF of (1.3b) exhibits a certain amount of universal behavior,[5b] but it is not clear how to express ΔF in terms of the model parameters of the continuum TP model. Previous RG calculations[6-9] have focused on the "universal" $n^{\gamma-1}$ contribution to the free energy in (1.1b) and dismiss the dominant "nonuniversal" μ/q term in (1.3b) because of its strong dependence on lattice details. But of course the $(\mu/q)^n$ contribution *must* be included in any meaningful analysis involving the free energy, regardless of whether a universal description exists or not.

A knowledge of ΔF and its dependence on temperature, molecular weight, molecular architecture, the presence of interacting surfaces, etc., is important in understanding, among other phenomena, the collapse of isolated polymers in poor solvents, the partitioning of polymers between different liquid phases, and the forces between polymer-coated surfaces. The calculation of ΔF also raises some fundamental mathematical issues that are interesting in their own right. Conventionally RG calculations simply ignore certain nonuniversal, "singular" contributions to ΔF. Here, as a first step in correcting this deficiency of the theory, we show that the known scaling behavior of ΔF for lattice chains and the requirement of consistency of the theory with lattice chain scaling behavior permit the retention and interpretation of these previously neglected terms. Our calculations with the TP model are reasonably consistent with lattice data for a variety of three- and two-dimensional lattices, although the systematics of the computational scheme remains to be checked in higher order calculations.

Section 2 examines lattice data for the change of free energy between self-avoiding and random walk chains. It is established that ΔF indeed exhibits some degree of universality as μ/q is found to be roughly constant for lattices of a given dimension. Encouraged by this empirical observation, we introduce the excluded-volume model for a continuous Gaussian chain in section 3. A cutoff is retained to avoid unphysical self-intersection of the polymer segments and is broadly intended to model the finite monomer size effects of discrete models. The change of

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Table I
Quasi-Universality of μ/q for Self-Avoiding Walk μ

lattice	q	d	μ^a	μ/q	$\mu/q \approx d/(d+1)^b$
honeycomb	3	2	1.3478	0.615	0.667
square	4	2	2.6385	0.660	0.667
triangular	6	2	4.1520	0.692	0.667
diamond	4	3	2.8792	0.720	0.750
cubic	6	3	4.6838	0.781	0.750
BCC	8	3	6.5295	0.816	0.750
FCC	12	3	10.0355	0.836	0.750
hypercubic	4	2	2.6385	0.660	0.667
	6	3	4.6838	0.781	0.750
	8	4	6.7680	0.846	0.800
	10	5	8.8313	0.883	0.833
	12	6	10.877	0.906	0.857
	∞	∞	$q - 1 \sim 2d - 1^c$	$(q-1)/q \sim 1^c$	1

[a] Reference 37. [b] Equation 2.1. [c] For high dimension we should recover the Cayley tree result $\mu \rightarrow q - 1$ of ref 39.

free energy ΔF is evaluated within the TP model in section 4, and section 5 considers the generalization of these calculations to polymers of various branching architectures and to polymers near surfaces.

2. Approximate Constancy of μ/q for Self-Avoiding Walks

The effective coordination number μ for self-avoiding walks and the lattice coordination number q are strongly dependent on the particular lattice. However, their *ratio* μ/q is roughly *constant* for a given dimensionality d, as displayed by the data in Table I. The trend in Table I is reasonably well reproduced by the relation (see Appendix A)

$$\mu/q \approx d/(d+1) \tag{2.1}$$

which is similar to the phenomenological relation (Appendix A)

$$(1/p_c^{\,B})/q \approx (d-1)/d \tag{2.2}$$

relating the bond percolation threshold $p_c^{\,B}$ to the dimensionality of space and q. The existence of the near (or quasi-) universality of μ/q suggests that a corresponding nearly universal theoretical description of ΔF may exist. The following sections are, therefore, directed toward calculating ΔF with the two-parameter (TP) model of excluded volume and renormalization group methods.

3. The Model

A Gaussian chain model represents the flexible polymer backbone, while the two-body interactions are described with a delta-function pseudopotential. The phenomenological parameters in this coarse-grained model are complicated functions of the detailed microscopic polymer geometry and structure; however, the nature of these functions is not required, since the final expressions treat all such parameters empirically.

The continuous chain has a configuration specified by the position $\mathbf{R}(\tau)$ of the chain segment at a contour distance τ along the chain. The bare dimensionless configuration Hamiltonian H/k_BT of the two-parameter model[10-12] is given by

$$H/k_BT = H_0 + H_1 \tag{3.1}$$

where

$$H_0 = (d/2l)\int_0^{N_0} d\tau \, |d\mathbf{R}(\tau)/d\tau|^2 \tag{3.2a}$$

and

$$H_1 = (\beta_2^{\,0}/2l^2)\int_0^{N_0} d\tau_2 \int_0^{N_0} d\tau_1 \, \delta[\mathbf{R}(\tau_1) - \mathbf{R}(\tau_2)] \qquad |\tau_2 - \tau_1| \geq a \tag{3.2b}$$

Here $\beta_2^{\,0}$ is a binary cluster integral, analogous to the binary cluster integral in the theory of imperfect gases, N_0 is the "bare" length of the chain, a is a cutoff to remove monomer self-interactions, and l is the effective (Kuhn) step length of the Gaussian chain. Higher order contributions are not required since dimensional analysis shows them to be negligible for dimensions $d \gtrsim 3$ and for N_0 arbitrarily large. A special situation exists for ternary[13,14] interactions in three dimensions, and the influence of these is discussed later.

It is convenient to rewrite (3.2) in terms of dimensionless variables through

$$\mathbf{r}(x) = (d/\langle \mathbf{R}^2 \rangle_0)^{1/2}\mathbf{R}(\tau), \qquad x = \tau/N_0 \tag{3.3}$$

where $\langle \mathbf{R}^2 \rangle_0 = N_0 l = n_0 l^2$ is the Gaussian chain mean-square end-to-end vector. Equation 3.3 converts H_0 and H_1 into

$$H_0 = (1/2)\int_0^1 dx \, |d\mathbf{r}(x)/dx|^2 \tag{3.4}$$

$$H_1 = (1/2!)z_2^{\,0}\int_0^1 dx_2 \int_0^1 dx_1 \, (2\pi)^{d/2}\delta[\mathbf{r}(x_1) - \mathbf{r}(x_2)] \qquad |x_2 - x_1| \leq a/N_0 \tag{3.5a}$$

with $z_2^{\,0}$ given by

$$z_2^{\,0} = (d/2\pi l^2)^{d/2}\beta_2^{\,0} n_0^{\,\epsilon/2} \tag{3.5b}$$

where $\epsilon = 4 - d$.

The unnormalized probability distribution for the chain ends is described by the path integral

$$G(\mathbf{R}/\langle \mathbf{R}^2 \rangle_0^{1/2}, z_2^{\,0}) = \int_{\mathbf{r}(0)=0}^{\mathbf{r}(1)=\mathbf{r}} D[\mathbf{r}(x)] \exp(-H/k_BT) \tag{3.6a}$$

where $D[\mathbf{r}(x)]$ is the conformational measure and the limits on the integral denote the fixed ends of the chain at $\mathbf{r}(0) = 0$ and $\mathbf{r}(1) = \mathbf{r}$. The partition function of the chain is evaluated from G through the integral

$$Q = \int d^d\mathbf{R} \, G(\mathbf{R}/\langle \mathbf{R}^2 \rangle_0^{1/2}, z_2^{\,0}) \tag{3.6b}$$

A perturbation series in the excluded volume interactions is generated by expanding $\exp(-H_1)$ in (3.6a) formally in a Taylor expansion in $z_2^{\,0}$. Expansions of this kind are given in the next section.

4. Calculation of the Partition Function

The free energy change ΔF of F(Gaussian flexible chain due to excluded volume interactions is evaluated from the configurational partition function Q through the relation

$$F(\text{SAW}) - F(\text{Gaussian chain}) = \Delta F = -k_BT \ln Q \tag{4.1}$$

where the zero of the free energy is chosen so that F(Gaussian chain) = 0.

A. Bare Perturbation Theory. Expanding the interaction term $\exp[-H_1(z_2^{\,0})]$ in (3.6a) as $1 - H_1 + \mathcal{O}(H_1^{\,2})$ produces the "bare" cutoff TP perturbation series

$$Q_B(a/N_0, z_2^{\,0}) = 1 + z_2^{\,0}[2/\epsilon(1 - \epsilon/2) - (a/N_0)^{-1+\epsilon/2}/(1 - \epsilon/2) - (2/\epsilon)(a/N_0)^{\epsilon/2}] + \mathcal{O}[(z_2^{\,0})^2] \tag{4.2}$$

An alternative calculational scheme, the method of dimensional regularization,[2] neglects the cutoff in (3.2) from the outset. This process effectively discards some terms involving a/N_0 in the preturbation expansion for Q_B, while others are converted to poles in ϵ. This purely formal mathematical procedure gives the perturbation expansion

$$Q_B(\text{dimensional regularization}) \equiv Q_B^{DR} = 1 + 2z_2^0/\epsilon(1 - \epsilon/2) + \mathcal{O}[(z_2^0)^2] \tag{4.3}$$

which appears, for example, in the work of des Cloizeaux[7] and Oono et al.[6] The Q_B^{DR} of (4.3) is perfectly adequate, however, for calculating the exponent γ and certain universal prefactor discussed below.

The renormalization group methods for analyzing (4.2) or (4.3) introduce additional expansions in ϵ to convert these equations, respectively, into

$$Q_B(a/N_0, z_2^0) = 1 + z_2^0[1 + (N_0/a) - \ln (a/N_0) + \mathcal{O}(\epsilon)] + \mathcal{O}[(z_2^0)^2] \tag{4.2a}$$

$$Q_B^{DR} = 1 + z_2^0[(2/\epsilon) + 1 + \mathcal{O}(\epsilon)] + \mathcal{O}[(z_2^0)^2] \tag{4.3a}$$

The term in $2/\epsilon$ in (4.3a), which is singular for $\epsilon \to 0$, corresponds to the $\ln (a/N_0)$ contribution in (4.2a), which is singular for $a \to 0$, while the nonsingular factors of z_2^0 are identical in both equations. An important difference arises from the N_0/a factor in (4.2a), which has no counterpart in (4.3a). The latter term may be shown to provide a "nonuniversal" contribution to the free energy, and it is generally discarded as a "mass subtraction" term in both the cutoff and dimensional regularization methods. Our present calculation uses the cutoff theory to calculate the free energy, and we retain the N_0/a contribution under the important condition that a is a strictly finite, viz, $a \geq l$.

It is convenient to factor Q_B of (4.2) into two portions T_B and $\delta\mu_B$, which after renormalization produce the universal factor T_R and the "nonuniversal" factor $\delta\mu_R$ that contributes to μ/q of (1.3b) in the self-avoiding walk limit. Thus, we write

$$Q_B = \delta\mu_B T_B \tag{4.4a}$$

with T_B and $\delta\mu_B$ given respectively by

$$T_B(a/N_0, z_2^0) = 1 + z_2^0[2/\epsilon(1 - \epsilon/2) - (2/\epsilon)(a/N_0)^{\epsilon/2}] + \mathcal{O}[(z_2^0)^2] \tag{4.4b}$$

$$\delta\mu_B = 1 - z_2^0(a/N_0)^{-1+\epsilon/2}/(1 - \epsilon/2) + \mathcal{O}[(z_2^0)^2] \tag{4.4c}$$

B. Renormalization of T_B. The renormalization of T_B follows standard procedures, so our discussion here is confined to a minimal discussion of the recipe for calculating the exponent γ. First, a dimensionless coupling constant u_2^0 is introduced through an alternate definition of z_2^0 as

$$z_2^0 = u_2^0(2\pi N/L)^{\epsilon/2} \tag{4.5}$$

with L a phenomenological length scale. Introducing (4.5) into (4.4b) and expanding to order ϵ give

$$T_B = 1 + u_2^0[1 + \ln (2\pi N_0/L) + \ln (L/2\pi a)] + \mathcal{O}(\epsilon^2) \tag{4.6a}$$

To extend the perturbation expansions of (4.6) to three-dimensions, the bare quantities T_B, N_0, and u_2^0 are renormalized to T_R, N, and u_2, respectively, through the relations $T_R = Z_Q T_B$, $N = Z_N N_0$, and $u_2 = Z_u^{-1}u_2^0$. The renormalization constants Z_Q, Z_N, and Z_u are defined as power series in u_2 of the form $Z_{(p)} = 1 + \sum_{i=1}^{\infty} a_i^{(p)} u_2^i$, and the coefficients $a_i^{(p)}$ are determined by the requirement that the terms in $\ln (L/2\pi a)$ be eliminated to each order of u_2 in renormalized perturbation expansions. Without going into details, which are provided elsewhere,[2,6,9] we find that the renormalized perturbation series for T_R, after introducing the renormalization constants into (4.6), becomes

$$T_R = 1 + u_2[1 + \ln (2\pi N/L)] + \mathcal{O}(\epsilon^2) \tag{4.6b}$$

The scaling behavior of the renormalized theory as a function of the excluded volume interaction is dictated by the renormalization group equation, which (again omitting details) enables the reexponentiation of (4.6b) to the crossover form

$$T_R = [1 + u_2(\bar{z})](2\pi N/L)^{u_2(\bar{z})} + \mathcal{O}(\epsilon^2) \tag{4.7}$$

where $u_2(\bar{z})$ is a function of a renormalized analogue of the z_2^0 parameter, denoted $\bar{z}$, that to first order in ϵ has the form[1,2]

$$u_2(\bar{z}) = u_2^*[4\bar{z}/(6 - d)(d - 2)u_2^*]/[1 + 4\bar{z}/(6 - d) \times (d - 2)u_2^*] + \mathcal{O}(\epsilon^2) \tag{4.8}$$

The quantity u_2^* is the fixed point or scaling limit value of u_2 and is given by

$$u_2^* = \epsilon/8 + \mathcal{O}(\epsilon^2) \tag{4.8a}$$

It is convenient for the discussion below to define a variable λ_2 and an exponent γ through respectively the equations

$$\lambda_2 = u_2(\bar{z})/u_2^* \tag{4.8b}$$

and

$$T_R \sim N^{\gamma-1} \tag{4.8c}$$

From (1.1b) and (4.7) and the definitions (4.8b) and (4.8c) the effective exponent $\gamma - 1$ in the region of finite $\bar{z}$ (the crossover region) is seen to be a function of the excluded-volume interactions

$$\gamma(\bar{z}) - 1 = u_2^*\lambda_2 + \mathcal{O}(\epsilon^2) \tag{4.9a}$$

while in the self-avoiding ($\bar{z} \to \infty$) and Gaussian chain ($\bar{z} \to 0$) limits respectively it takes the well-known values

$$\gamma(\bar{z} \to \infty) - 1 = \epsilon/8 + \mathcal{O}(\epsilon^2) \tag{4.9b}$$

$$\gamma(\bar{z} \to 0) - 1 = 0 \tag{4.9c}$$

A second-order calculation gives the more accurate prediction[15] (see subsection E)

$$\gamma(\bar{z} \to \infty) - 1 = \epsilon/8 + (13/4)(\epsilon/8)^2 + \mathcal{O}(\epsilon^3) \tag{4.9d}$$

C. Analysis of $\delta\mu_B$. There is no obvious systematic scheme for the renormalization (resummation) of the series for $\delta\mu_B$, so two different lines of reasonaing are followed in parallel to explore a range of possibilities for addressing this problem. Subsequently, these possibilities are tested against lattice data.

The simplest way to proceed is to ϵ-expand the series for $\delta\mu_B$ and to assume the series can be renormalized in the same way as the series for T_B (4.6a) with the only difference that the cutoff is retained as a purely phenomenological parameter. Expanding (4.4c) in ϵ gives

$$\delta\mu_{B,\epsilon} = 1 - u_2^0(N_0/a) + \mathcal{O}(\epsilon^2) \tag{4.10a}$$

where the ϵ subscript indicates that ϵ-expansion has been employed. Next we renormalize u_2^0 and N_0 in the standard fashion to obtain the renormalized perturbation series

$$\delta\mu_{R,\epsilon} = 1 - u_2(N/a) + \mathcal{O}(\epsilon^2) \tag{4.10b}$$

An alternate procedure involves *avoiding* the ϵ-expansion procedure altogether and considers the $\delta\mu_B$ series as an expansion in the binary cluster integral β_2^0 of (3.2b). This approach converts (4.4c) into

$$\delta\mu_B = 1 - s(\beta_2^0/l^d)n_0 + \mathcal{O}[(\beta_2^0)^2] \qquad (4.11a)$$

$$s \equiv (d/2\pi)^{d/2}(l/a)^{1-\epsilon/2}/(1 - \epsilon/2) \qquad (4.11b)$$

This method is appropriate provided the series for $\delta\mu_B$ contains neither poles in ϵ or ln (a/L) terms requiring renormalization. An alternative decimation procedure, based on a Wilson-style renormalization group analysis of Ma,[16] leads to a form similar to (4.11) and is described in Appendix B.

Some guidance on how to treat the series (4.10b) and (4.11a) is provided by the rigorous lattice calculations of Hammersley[3] [see (1.3b)] on the limiting value of $\delta\mu_B$ and by the continuum model calculations of des Cloizeaux,[7] which indicate that Q has the self-avoiding walk form

$$Q \sim \exp(-a_c n_0) \qquad (4.12)$$

where a_c is an unspecified nonuniversal parameter that obviously must depend on the excluded-volume interaction. These calculations imply that ΔF is proportional to n for $n \to \infty$, so that

$$-\Delta F/nk_BT \to \text{constant}, \qquad n \to \infty \qquad (4.13)$$

which is just a statement of the extensive character of the free energy change. We now inquire whether anything can be deduced about the constant in (4.13) based on the series (4.10b) and (4.11a).

Consistent with (4.13) we rewrite (4.10b) and (4.11a) as[17]

$$\delta\mu_{R,\epsilon} = \exp[-u_2^*(l/a)n\lambda_2] + \mathcal{O}(\epsilon^2) \qquad (4.14)$$

$$\delta\mu_B = \exp[-s(\beta_2^0/l^d)n_0] + \mathcal{O}[(\beta_2^0)^2] \qquad (4.15)$$

respectively. The magnitudes of $\delta\mu$ calculated from (4.14) and (4.15) in the long-chain SAW limit may now be compared against lattice data.

First, for purposes of a qualitative understanding, we take $a = l$ in (4.14) since the constraint against self-intersection occurs on this scale in lattice models. This choice and the conditions of fully developed excluded volume and very long chains (which imply $u_2^*\lambda_2 \to u_2^*$) lead to

$$-\Delta f \equiv -\Delta F/nk_BT = u_2^* + \mathcal{O}(\epsilon^2), \qquad a = l,\ n \to \infty,\ \epsilon \geq 0 \qquad (4.16)$$

where for now we neglect the subdominant contribution from the T_R part of the free energy. Introducing first and second order in ϵ estimates for u_2^* in (4.14), taking $a = l$, and specializing to $d = 3$ give

$$\exp(-\Delta f) = \exp(-0.125) = 0.88 \qquad \text{(first order)} \qquad (4.17)$$

$$\exp(-\Delta f) = \exp(-0.207) = 0.81 \qquad \text{(second order)} \qquad (4.18)$$

The long-chain limit (1.3b) for lattices yields $\exp(-\Delta f) \sim \mu/q$, whose value as given in Table I compares favorably with the estimates of (4.17) and (4.18). Since a is only of the order of l, the estimates (4.17) and (4.18) are quite reasonable and suggest that a residual (possibly nonuniversal) positive proportionality factor on the order of unity might account for the observed variations of ΔF in Table I (see discussion below). The prediction (4.17) is also given by Kosmas,[18] who employs the implicit assumption $a = l$ in his discrete formulation of the TP model. The zero of the free energy, however, is chosen differently in his calculations.

Table II
Theoretical Estimates vs. Lattice Data for Self-Avoiding Walk μ/q

lattice	d	β_2/l^d	μ/q[a]	μ/q(estimate)[b]
3-choice 120°	2	1.30	0.615	0.582
4-choice square	2	1.00	0.660	0.660[c]
6-choice 60°	2	0.866	0.692	0.697
4-choice tetrahedral	3	1.54	0.720	0.684
6-choice simple cubic	3	1.00	0.781	0.781[c]
8-choice BCC	3	0.770	0.816	0.827
12-choice FCC	3	0.707	0.836	0.840

[a] Reference 40. [b] Calculated with (4.26). [c] Specified by choice of s.

We now turn to (4.15), which avoids ϵ-expansion, to see if it can provide a more quantitative and universal description of ΔF. The value of a [or equivalently s in (4.15)] is taken as a phenomenological parameter to be *fixed* once and for all using a *single* known value of μ/q for a lattice of a given dimension. The value of β_2^0/l^d for long chains in the self-avoiding limit should simply be the lattice cell volume in units of the lattice spacing.[19] Values of the lattice cell volumes are listed in Table II for several lattices. Taking square and cubic lattices as our standard, where the lattice cell volumes are conveniently unity, and using the μ/q values listed in Table I lead to

$$s(d{=}3) = 0.247 \qquad (4.19a)$$

$$s(d{=}2) = 0.416 \qquad (4.19b)$$

Once s is fixed, as in (4.19), there are no longer any free parameters in (4.11b), and the predictions from (4.15) and (4.18)–(4.19b) are indicated in Table II for several two- and three-dimensional lattices. The trend in μ/q is well produced by (4.15), but there are somewhat larger errors for small q. Some of this error may arise because of the neglect of ternary interactions.[13,14]

D. Role of Ternary Interactions and General Models of Interacting Walks. Polymer properties in $d = 3$, in principle, may be influenced by ternary interactions,[13,14] but a precise treatment of these effects is currently possible only near the Θ point. Calculations similar to those in this section with ternary interactions included could provide at the Θ point a contribution to the nonuniversal portion of the partition function $\delta\mu_B$ of the form ($d = 3 - \epsilon'$)

$$\delta\mu^{\Theta}_{R,\epsilon} = 1 - (\text{constant})u_3(N/a) + \mathcal{O}[(\epsilon')^2] \qquad (4.20a)$$

where u_3 is the renormalized ternary interaction parameter.[14] The proportionality of ΔF to n would likewise imply the exponentiation

$$\delta\mu^{\Theta}_{R,\epsilon} = \exp[-(\text{constant})u_3(N/a)] \qquad (4.20b)$$

Currently, values of u_3 appropriate to different lattices are unknown, and it is unclear how to extend (4.20b) into the realm of *both* u_2 and u_3 large. However, experience with a wide range of polymer properties indicates that reduced ratios of these properties, i.e., their magnitudes relative to Θ-point values, are well explained by taking the ratios to depend only on (an effective shifted) u_2. This suggests, but definietly does not prove, that the contribution from ternary interactions can be included by multiplying the right-hand side of (4.14) or (4.15) by the right-hand side of (4.20b), a process which, if u_3 is lattice-dependent, introduces an additional nonuniversality into the problem.

The possible role of ternary interactions raises some further questions. The treatment of the free energy in terms of binary interactions alone describes the crossover between Gaussian and self-avoiding walks, but many

Table III
Enhancement Exponent γ in $Q \sim (\mu/q)^n n^{\gamma-1}$

	$\gamma - 1$ (self-avoiding walk)[a]	$\gamma - 1$ (Gaussian chain)	prefactor coeff, a_T
linear	$\epsilon/8 + (13/4)(\epsilon/8)^2 + \mathcal{O}(\epsilon^3)$	0	1
f-arm starm	$(\epsilon/16)[2 - (f-1)(f-2)] + \mathcal{O}(\epsilon^2)$	0	$(3f + f^2)/4 - f(f-1) \ln 2$
hyperloops(variable $d_\perp$)		$-d_\perp/2$	
ring, $d_\perp = d$	$-d/2 - \epsilon/4 + \mathcal{O}(\epsilon^2)$	$-d/2$	2
$d_\parallel = 2$, $d_\perp = d - 2$	$(2 - d)/2 + \mathcal{O}(\epsilon^2)$	$(2 - d)/2$	2
"loop chain", $d_\perp = 1$	$-(1/2) + \epsilon/16 + \mathcal{O}(\epsilon^2)$	$-1/2$	$(2 \ln 2 + 1)/2$
$d_\perp = 2$	$-1 + \mathcal{O}(\epsilon^2)$	-1	1
chain attached at one end to impenetrable reflecting surface	$3\epsilon/16 + (27/8)(\epsilon/8)^2 + \mathcal{O}(\epsilon^3)$	0	$2 + \pi/3^{1/2}$

[a] See ref 9 for listing of the original references.

Monte Carlo studies employ more sophisticated models where residual interactions at the Θ point and perhaps contributions like (4.20b) are also included. The free energies of these Monte Carlo models are, therefore, somewhat different, as they do not use the unrestricted random walk limit to define the zero of energy.

Also, when self-avoiding lattice walks are biased by sufficient nearest-neighbor attractions, the resultant chains mimic the statistics of Gaussian chains to a good approximation,[14] but the free energy should be closer to that of a nonreversing random walk with $C_n \sim (q-1)^n$ rather than to that of a random walk.[20] Thus, we do not expect $[F(\mathrm{SAW}) - F_\Theta]/k_BT$ to be proportional to $\ln (\mu/q)$. (The nonreversing model gives $\ln [\mu/(q-1)]$.) One phenomenological approach to the problem is to let a be an empirical parameter that is determined by comparison with experiment. If (4.20b) is of the correct form, such a procedure subsumes the unknown u_3 into an effective a.

The cutoff parameter appears in two-parameter model calculations of the free energy, but it also enters into perturbation calculations in the form of finite chain length corrections. It is not clear whether these two nonuniversal manifestations of a are related, but the finite chain length corrections have been studied both by Bruns,[21] through the effects of varying potentials on the binary interaction perturbation expansion, and by Barrett,[22] through the application of the Domb–Joyce model to several lattices. Their perturbation calculations yield the following general form for the mean-square end-to-end distance $\langle \mathbf{R}^2 \rangle$ in $d = 3$ [see (4.4b)]

$$\langle \mathbf{R}^2 \rangle = \langle \mathbf{R}^2 \rangle_0 \{1 + [4/3 - An^{-1/2} + \mathcal{O}(n^{-1})] z_2{}^0 + \mathcal{O}[(z_2{}^0)^2]\}$$

where $\langle \mathbf{R}^2 \rangle_0 = N_0 l$ and the $z_2{}^0$ parameter is defined in terms of the potentials and lattice parameters, respectively. The coefficient A depends on the potential, but within the Domb–Joyce model it is constant to within about ±4% deviation from an average value. It would be interesting to determine whether this A is in some sense related to the a required in (4.14) or (4.15). This would help explain the lattice dependence of μ since two-parameter model calculations yield a similar form for $\langle \mathbf{R}^2 \rangle$, the coefficient of $z_2{}^0$ in $d = 3$ being given by[14]

$$4/3 - 2(a/N_0)^{1/2}[1 + \mathcal{O}(a/N_0)]$$

which is of the same form as in lattice studies. Although there is no a priori reason for the phenomenological cutoff dependences of μ and finite chain length corrections to be related aside from in the two-parameter model, a finding that the same phenomenological a parameter can fit several different properties would, of course, be quite interesting. If this type of relation were found, then it would enable the unambiguous determination of a for each specific microscopic model of binary excluded volume.

E. Constrained Partition Functions. The free energy becomes an important polymer property for polymers in confined spaces and near interacting surfaces. Lattice Monte Carlo calculations suggest that μ in the self-avoiding walk limit is independent of the presence of a noninteracting plane boundary and is independent of polymer architecture for light branching (e.g., rings, stars, etc., which remain in the same universality class as linear polymers). Thus, a useful check of the theory involves the verification that μ in this limit is unchanged by the presence of boundaries and light branching. The representation (4.14) is, however, more general and applies to the crossover regime between the random and self-avoiding walk limits. The universal exponent γ, on the other hand, is affected by boundaries and polymer architecture. We illustrate the theory in this subsection with calculations of μ and γ for hyperloops[9] (chains with both ends confined to a $d_\parallel$-dimensional hypersurface), ring, star, and comb polymers,[9,23] and polymers at impenetrable surfaces. Some of the results are summarized in Table III.

(1) Hyperloops and Ring Polymers. Defining $d_\perp = d - d_\parallel$, we calculate the partition function for a hyperloop as

$$Q(\text{hyperloop}) = (d/2\pi \langle \mathbf{R}^2 \rangle_{0,f})^{d_\perp/2} \{1 - z_2{}^0 [B(-1+\epsilon/2; 2-d_\perp/2) - B_{a/N_0}(-1+\epsilon/2; 2-d_\perp/2)]\} + \mathcal{O}[(z_2{}^0)^2] \quad (4.21a)$$

where B is the beta-function and $B_{a/N_0}(x,y)$ is the incomplete beta-function. The Gaussian chain limit of (4.21a) is

$$Q(\text{hyperloop}) \sim n^{-d_\perp/2}, \qquad z_2{}^0 = 0 \quad (4.21b)$$

The beta-function in (4.21a) B_{a/N_0} can be rewritten as[24]

$$B_{a/N}(-1+\epsilon/2; 2-d_\perp/2) = [(a/N)^{-1+\epsilon/2}/(-1 + \epsilon/2)]\, {}_2F_1(-1+\epsilon/2, -1+d_\perp/2, \epsilon/2; a/N_0) \quad (4.22a)$$

where the hypergeometric function has the leading behavior, as $a/N_0 \to 0$ of

$$ {}_2F_1(-1+\epsilon/2, -1+d_\perp/2, \epsilon/2; a/N_0) = 1 + \mathcal{O}(a/N_0) \quad (4.22b)$$

When terms of order $(a/N_0)^{\epsilon/2}$ in (4.22a) are neglected, which vanish as $N_0 \to \infty$, eq 4.22a becomes

$$Q(\text{hyperloop}) = (d/2\pi \langle \mathbf{R}^2 \rangle_0)^{d_\perp/2} [1 - z_2{}^0 (a/N_0)^{-1+\epsilon/2}/(1 - \epsilon/2) + ...][1 - z_2{}^0 B(-1+\epsilon/2; 2-d_\perp/2) + ...] \quad (4.22c)$$

or after use of (4.4c), we have

$$Q(\text{hyperloop}) = (d/2\pi \langle \mathbf{R}^2 \rangle_0)^{d_\perp/2} \delta\mu_B [1 - z_2{}^0 B(-1+\epsilon/2; 2-d_\perp/2) + ...] \quad (4.22d)$$

A ring polymer is a hyperloop[9] in the limit that $d_\parallel \to 0$, so both chain ends are restricted to be at a point. The

$d_\perp = d$ limit of the beta-function in (4.22d) is ϵ-expanded as

$$B(-1+\epsilon/2;\epsilon/2) = (-4/\epsilon)(1-\epsilon/2) + \mathcal{O}(\epsilon) \qquad (4.22\text{e})$$

Renormalization of (4.22d) with (4.22e) follows just as in subsection B and products the final result in the generic form

$$T_{\mathrm{R}j} = (2\pi N/L)^{(\gamma_j-1)\lambda_2}(1 + a_j u_2{}^*\lambda_2) + \mathcal{O}(\epsilon^2) \qquad (4.23)$$

where the good solvent limit exponents γ_j and prefactor coefficients for each architecture or boundary situation are listed in Table III and where $u_2{}^*$ and λ_2 are defined in (4.8b) and (4.8c), respectively. Similarly, the full renormalized partition function for hyperloops is

$$Q(\text{hyperloop}) = (d/2\pi\langle\mathbf{R}^2\rangle)^{d_\perp/2}\delta\mu_{\mathrm{R}}(2\pi N/L)^{[\gamma(\text{hyperloop})-1]\lambda_2} \times [1 + a(\text{hyperloop})u_2{}^*\lambda_2] + \mathcal{O}(\epsilon^2) \qquad (4.24)$$

(2) Star and Branched Polymers. The same analysis applies for lightly branched polymers where the renormalized total partition function has the form

$$Q(\text{branched}) = \delta\mu_{\mathrm{R}}T_{\mathrm{R}}(\text{branched}) \qquad (4.25)$$

Kosmas[23] has recently calculated γ(comb), so it is not given here. The results for star polymers with arms of equal length N are presented in Table III. Subdominant corrections of the form $(a/N_0)^{\epsilon/2}$ are again neglected.

(3) Polymer Near a Surface. For the simplest example of a polymer terminally attached to a reflecting impenetrable planar surface ($d_\perp = 1$, $d_\parallel = d - 1$) the partition function follows from the calculations of Freed[25a] and Nemirovsky and Freed[25b] as

$$Q(\text{surface}) = \delta\mu_{\mathrm{R}}(2\pi N/L)^{\gamma-1}[1 + a(\text{surface})u_2{}^*\lambda_2] \qquad (4.26\text{a})$$

where $\gamma - 1$ and a(surface) are given in Table III. A particularly interesting generalization involves allowing the chain end to be fixed at some distance $R_\perp{}^0$ normal to the surface rather than at the surface. With the definition $r_\perp{}^0 \equiv R_\perp{}^0(d/\langle\mathbf{R}^2\rangle_0)^{1/2}$, such a calculation yields

$$a(\text{surface}(r_\perp{}^0)) = a(\text{surface}(r_\perp{}^0{=}0)) + \mathcal{O}(r_\perp{}^0)^2, \qquad r_\perp{}^0 \ll 1 \quad (4.26\text{b})$$

When $r_\perp{}^0$ becomes of order of unity, Q(surface) must approach that for a free chain without the surface, so the exponent γ must cross over from γ(surface) at $r_\perp{}^0 \to 0$ to γ for a free chain for $r_\perp{}^0 \gg 1$. This type of crossover is fairly unique and has recently been studied by Nemirovsky et al.[26a] for related problems in critical phenomena.

(4) Polymers Confined between Parallel Plates. A considerable amount of experimental interest has recently centered on studies of the forces between polymer-coated surfaces, and the theoretical description of this situation requires the calculation of (nonuniversal) free energies. When the plate separations are sufficiently large and/or the polymer concentrations in the interaction region are sufficiently low, renormalization group methods may be useful for calculating the universal part of the free energy. The simple example below, which considers a particular limit of a polymer between two plates in minimal contact with the surface, serves to demonstrate that the dominant nonuniversal portion $\delta\mu'_{\mathrm{R}}$ generally depends on the interplate separation and that its contribution to the forces may therefore be rather important. A higher degree of polymer–surface contacts is expected to greatly alter $\delta\mu_{\mathrm{R}}'$ because of the effective change of dimensionality when the polymer becomes adsorbed onto the surface.

The partition function Q(plates) for a polymer lying between impenetrable reflecting parallel plates with separation κ may be evaluated as[26b]

$$Q(\text{plates}) = \delta\mu_{\mathrm{R}}'\left(1 + \frac{\epsilon}{8}\right) \times \left(\frac{2\pi N}{L}\right)^{\epsilon/8}\left[1 + \frac{\epsilon}{2}\left(\frac{\pi}{2}\right)^{1/2}\frac{N^{1/2}}{\kappa}\right], \qquad \langle\mathbf{R}^2\rangle/\kappa^2 < 1 \qquad (4.27\text{a})$$

where the renormalized connectivity constant $\delta\mu_{\mathrm{R}}'$ differs from that in eq 4.10b by the presence of an added small dependence on κ

$$\delta\mu_{\mathrm{R}}' = 1 - u_2(N/a)[1 + (2\pi a)^{1/2}/\kappa], \qquad N^{1/2}\kappa^{-1} < 1 \qquad (4.27\text{b})$$

The restriction to $\langle\mathbf{R}^2\rangle < \kappa^2$ (or equivalently $N^{1/2} < \kappa$) appears in (4.27) because otherwise the finite size correction factor in the square brackets of (4.27a) would be an expansion in the large parameter $\langle\mathbf{R}^2\rangle^{1/2}/\kappa$. In addition, the standard Gaussian chain continuum model (3.2a) does not approach the correct physical behavior for $\kappa \sim \mathcal{O}(l)$. This technical problem is discussed in ref 27.

(5) Interacting Surfaces. The algebra becomes considerably more complicated and, therefore, less transparent when there are interactions energies between the polymer and the surface. Calculations of this type for T_{R} of a planar impenetrable surface and T_{R} of a planar penetrable surface as a function of the polymer–surface and polymer–polymer interactions have been carried out respectively by Nemirovsky and Freed,[25] Wang et al.,[28] and Douglas et al.,[27] so their results are not reproduced here.

5. Discussion

The two-parameter model is applied to the calculation of the free-energy change ΔF of a flexible polymer when fully developed excluded-volume interactions are present. The influence on ΔF of molecular architecture and proximity to a surface is also investigated.

"Universal" and "nonuniversal" contributions to ΔF are separated. The theoretical treatment of the "universal" contribution to ΔF involving the exponent γ is well-known. However, the "nonuniversal" contribution to ΔF, which explicitly depends on details of the lattice through a cutoff parameter, is not so readily handled. We discuss some ways of systematically studying this second and previously neglected free energy term. Our theoretical results are in quite good agreement with available numerical data.

The dominant contribution to ΔF for long chains is found to be independent of molecular geometry and the presence of a single surface. This conclusion is consistent with lattice calculations for self-avoiding walks which indicate the constancy of the self-avoiding walk lattice connectivity constant μ for lightly branched polymers (rings, stars, etc.)[29] and for polymers in the presence of a surface.[30] However, our theory provides predictions of the crossover dependence of an excluded-volume dependent connectivity constant between the Gaussian and self-avoiding walk limits, and these predictions remain to be tested against lattice calculations. Subdominant contributions to ΔF, associated with the portion of the partition function involving the exponent γ, depend very sensitively on molecular architecture, as is well-known from studies on the self-avoiding walk limit. Again, we evaluate the crossover dependence of γ for many cases.

Two competitive effects determine ΔF. As a consequence of interfering nearest neighbors, the principal effect of excluded volume on lattice polymers is to decrease the

Table IV
Estimates of μ^B/q

d	lattice type	series anal.[a]	Monte Carlo[a]	$\mu^B/q \approx (d-1)/d$[b]
3	SC	0.675	0.6680 ± 0.002	0.67
	BCC	0.700		0.67
	FCC	0.700	0.66	0.67
	HCP		0.672	0.67
	diamond		0.644	0.67
2	hypercubic	1/2 (exact)		1/2
3	hypercubic	0.66		2/3
4	hypercubic	0.776, 0.871		3/4
5	hypercubic	0.847		4/5
6	hypercubic	0.887		$5/7 \approx 0.83$
7	hypercubic	0.916		$6/7 \approx 0.85$

[a] Reference 35. [b] Reference 34.

"effective coordination number" of the lattice walk relative to that of a random walk. An analogous contribution emerges in the two-parameter model with a cutoff, although the explicit dependence of this contribution on the cutoff does not argue in favor of the universality that numerically is suggested to exist in some degree.

While short-range interferences drastically decrease the number of configurations, this effect is partially compensated by the swelling of the polymer, which increases the number of configurations. It is likely that this enhancement in the number of configurations due to swelling is related to the exponent γ, although a simple "geometric" interpretation for γ is not yet available.

The variation of γ with different constraints is worth summarizing. (For convenience we distinguish between the exponents of Gaussian and self-avoiding chains: henceforth γ_0 refers to the Gaussian chain, while γ continues to designate the self-avoiding chain). Table III shows that constraints on the kind of branching architecture (ring, star, etc.) have the effect of reducing γ. This effect is particularly strong for the formation of loops where both γ and γ_0 are reduced. Another example of a branched structure is the hyperloop, a loop constrained to return to a $d_\parallel$-dimensional surface where $d_\perp + d_\parallel = d$. Here γ and γ_0 depend strongly on $d_\perp$. For $d_\perp > 2$ ($2 < d < 4$) the exponent γ to order ϵ becomes *reduced* relative to γ_0, and for $d_\perp < 2$ there is an *increase* in γ relative to γ_0. Excluded-volume interactions thus diminish the probability of ring closure relative to Gaussian chains, but they actually *enhance* the probability of the chain looping back to a surface of dimension $d - 1$.

The influence of branching nodes on the number of polymer configurations is illustrated in the value of γ for f-arm stars where $\gamma_0 = 1$, independent of the number of arms. However, the presence of excluded volume strongly reduces the value of γ as the number of arms increases.

Boundaries alter the exponent γ in significant and subtle ways. For example, a reflecting (nonintereacting in the continuum model) impenetrable boundary has no influence on γ_0, but γ is actually *increased.* Surface curvature affects the magnitude of γ in a rather obvious way. This can be seen in a thought experiment where a polymer is imagined to be terminally attached at one end to an impenetrable sphere. In the limit of the sphere becoming much larger than the mean dimensions of the polymer, γ should equal the value obtained for an impenetrable plane. On the other hand, when the sphere radius is much smaller than the mean dimensions of the polymer, γ must equal the free chain value. Calculations by Wang et al.[28] describe the full crossover between these obvious limiting situations for Gaussian chains. The description is nontrivial ($\gamma \neq 1$) when there are surface interactions and constraints on loop formation onto the spherical surface.

Table V
Return Probability R

d	lattice	R	R(estimate)[b] $\approx 1/d$
3	SC	0.340 537[a]	0.33
	BCC	0.282 230	0.33
	FCC	0.256 328	0.33
	HCP	0.282 230	0.33
	diamond	0.256 328	0.33
4		0.2	0.25

[a] Reference 34. [b] Equation A.8.

The problems discussed above relate to the more general question of determining the variation of ΔF and γ with "surface irregularity". This question could be studied by considering polymers interacting with fractal objects,[31] and it encompasses a very broad and physically very important class of problems. For instance, a dispersion of some impurity or additive in a polymer solution can be thought of as a polymer interacting with a "fractal dust".[31] A theory of polymers interacting with fractals might bear on the same issue of colloid stability as colloid particles can be expected to have fractal dimensions that are different from those of the simple random coil polymer. Porous absorbents of chromatography columns can perhaps be approximated as fractal objects, while block copolymers and polymer mixtures, where the solvent quality varies for the different chemical species, can be considered as the interaction of a polymer (one of the chemical species) with a fractal object (the other chemical species). The study of this type of effect should perhaps begin with Gaussian chains and nonrandom fractals[31] where there is a good chance of determining exact solutions.

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Appendix A: Related Forms of Quasi-Universality

In the related field of percolation problems Broadbent and Hammersley[32] have proven the rigorous inequality

$$p_c^s \gtrsim p_c^B \gtrsim 1/\mu \tag{A.1}$$

where p_c^s and p_c^B are the site and bond percolation thresholds. Equality holds on a Cayley tree where[33]

$$p_c^s = p_c^B = 1/\mu = 1/(q-1) \tag{A.2}$$

corresponds to the expected result for high dimensionality. The precolation thresholds appear in (A.1) and (A.2) as effective coordination numbers, and accordingly we define

$$\mu^B \equiv (p_c^B)^{-1}, \qquad \mu^s \equiv (p_c^s)^{-1} \tag{A.3}$$

Vyssotsky[34] has proposed that

$$\mu^B/q \approx (d-1)/d \tag{A.4}$$

and a comparison of this prediction is given in Table IV for self-avoiding random walks on various lattices in several dimensions.[35] The concept of quasi-universality holds for μ^B/q, and the Vyssotsky-type relation provides a reasonable first approximation. Table I shows that the Vyssotsky-like relation (introduced here)

$$\mu/q \approx d/(d+1) \tag{A.5}$$

explains the dimensional dependence of μ/q reasonably well. Combining (A.4) and (A.5) provides the interesting approximate relation

$$(\mu/q)_d \approx (\mu^{\mathrm{B}}/q)_{d+1} \qquad \text{(A.6)}$$

relating μ and μ^{B} through a dimensional shift.

Another approximation, which is apparently more accurate than the Vyssotsky relation, is given by[35]

$$(\mu^{\mathrm{B}}/q) \approx 1 - \mathrm{R}, \qquad d > 2 \qquad \text{(A.7)}$$

where R is the return probability of a lattice random (Polya) walk to a point in $d > 2$ dimensions.[35] Equating (A.7) with (A.4) gives the coarse approximation

$$\mathrm{R} \approx 1/d, \qquad d > 2 \qquad \text{(A.8)}$$

A listing of return probabilities for various lattices is given in Table V. Montroll[36] has derived an asymptotic expansion for R on hypercubic lattices

$$\mathrm{R} = \frac{1}{2d}\left(1 + \frac{1}{d} + \frac{7}{(2d)^2} + \frac{35}{(2d)^2} + \ldots\right) \qquad \text{(A.9)}$$

to be compared with (A.8). Numerous other $1/d$ expansions for "nonuniversal" critical constants on cubic lattices are summarized by Gaunt.[37]

Appendix B: Decimation Approach

The nonuniversal cutoff dependent contributions to Q_{B} are shown in the main body of the paper to determine the magnitude of the quasi-universal ratio μ/q and may be studied in a somewhat different way. Following the work of Ma[16] on the free energy of lattice spin systems, we reformulate the related polymer problem in Fourier–Laplace space,[2] the role of a minimal distance being played by a cutoff ($\sim a^{-1/2}$) on high wave vectors. Working directly in $d = 3$ with the usual continuum model of section 3, the bare partition function Q_{B} is readily shown to be given by

$$Q_{\mathrm{B}} = 1 - z_2^{\,0} N_0^{-1/2} (2\pi)^{-3/2} L^{-1} s^{-2} \int \mathrm{d}^3k\, G_0(k,s) + \mathcal{O}[(z_2^{\,0})^2] \qquad \text{(B.1)}$$

where $G_0(k,s) = (\mathbf{k}^2/2 + s)^{-1}$ with $\mathbf{k}$ the momentum variable conjugate to $\mathbf{r}$ and s the Laplace variable conjugate to the contour length N_0. L^{-1} denotes the operation of taking the inverse Laplace transform. The integral over $\mathbf{k}$ in (B.1) is written explicitly as

$$I = \frac{4\pi^{3/2}}{\Gamma(3/2)} \int_0^{\Lambda} \mathrm{d}k\, k^2(k^2 + 2s)^{-1} \qquad \text{(B.2)}$$

where Γ is the gamma-function.

Q_{B} is calculated from (B.2) by successively thinning the degrees of freedom in the expression for I. In practical terms this means integrating out contributions to I from k values lying between Λ and Λ/h, where h is some positive number. After a first integration, this process is represented as

$$I = \frac{4\pi^{3/2}}{\Gamma(3/2)}\left[\int_{\Lambda/h}^{\Lambda} \mathrm{d}k\, k^2(k^2 + 2s)^{-1} + \int_0^{\Lambda/h} \mathrm{d}k\, k^2(k^2 + 2s)^{-1}\right] \qquad \text{(B.3)}$$

The first integral in the above equation contributes to μ/q while the second is used to evaluate $N^{\gamma-1}$. In this second integral k is rescaled as $k \to k/h$. The original range of integration is thus restored, but $I \to I' = I/h$ and $s \to s' = sh^2$. Then, I' is integrated as before, followed by the rescaling of k'. This process is continued till successive applications of the two-step transformation illustrated above leave the system unchanged, that is, take it to its fixed point. If the fixed point is reached after p interations, the nonuniversal part of Q_{B} that is used to calculate $\delta\mu_{\mathrm{B}}$ may be evaluated as

$$\delta\mu_{\mathrm{B}} = 1 - \frac{z_2 N^{-1/2}}{(2\pi)^{3/2}} \frac{4\pi^{3/2}}{\Gamma(3/2)} \sum_{i=1}^{p} \left[N\Lambda\left(1 - \frac{1}{h}\right)\frac{1}{h^{i-1}} - 2^{1/2} L^{-1} s^{-3/2} \tan^{-1} \frac{8sh^{i-1}(h-1)}{2\Lambda\left(1 + \dfrac{8sh^{2i-1}}{4\Lambda^2}\right)} \right] \qquad \text{(B.4)}$$

The above expression can be simplified by neglecting the second term in brackets since for large Λ (corresponding to small a) it yields corrections that are of order Λ^{-1}. Further by approximating the sum over i by an integral over i, we obtain

$$\delta\mu_{\mathrm{B}} = 1 - \frac{z_2 N^{-1/2}}{(2\pi)^{3/2}} \frac{4\pi^{3/2}}{\Gamma(3/2)} N\Lambda \left(\frac{1 - h^{-p+1}}{\ln h}\right)\left(1 - \frac{1}{h}\right) \qquad \text{(B.5)}$$

Further simplification is possible if it is supposed that $p \gg 1$ so that $h^{-p} \ll 1$. Also, in ref 14 it is suggested that $\Lambda \approx 1/2a^{1/2}$. Introducing these relations into eq B.5 transforms it to

$$\delta\mu_{\mathrm{B}} = 1 - \left(\frac{2}{\pi}\right)^{1/2} z_2 \left(\frac{l}{a}\right)^{1/2} \frac{1}{\ln h}\left(1 - \frac{1}{h}\right) n^{1/2} \qquad \text{(B.6)}$$

Equation B6 may be rewritten by using (3.5b) in terms of the cluster integral $\beta_2^{\,0}$ as

$$\delta\mu_{\mathrm{B}} = 1 - \frac{3^{3/2}}{(2\pi)^{3/2}} \left(\frac{2}{\pi}\right)^{1/2} \left(\frac{l}{a}\right)^{1/2} \frac{\beta_2^{\,0}}{l^3} n (\ln h)^{-1} (1 - 1/h) \qquad \text{(B.7)}$$

There is some arbitrariness in the choice of h, and one possibility is to assign it a value that eliminates the term in $(l/a)^{1/2}$. It this is done the numerical factor in (B.7) is calculated as 0.26, which is close to the value required of s in section 3 for agreement with numerical data. Alternatively, h may be chosen so that the agreement actually becomes exact for some lattice, and further predictions for other lattices can then be made on the basis of this result.

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Determination of Polymer–Solvent Interaction Parameter from Swelling of Networks: The System Poly(2-hydroxyethyl methacrylate)–Diethylene Glycol

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ABSTRACT: Poly(2-hydroxyethyl methacrylate) gels are prepared by cross-linking with various amounts of ethylene glycol dimethacrylate in diethylene glycol solvent. The degree of swelling of the networks in diethylene glycol is measured in the range $0 < v_2 < 0.35$ as a function of cross-link density and solvent content during cross-linking. Results of swelling measurements are used to determine the polymer–solvent interaction parameter χ of the system. An expression of the form $\chi = 0.49 - 0.25v_2$, where v_2 is the polymer volume fraction, is estimated for the investigated system at 25 °C, which is in agreement with Janáček and Ferry's results. The analysis of experimental data provides information about the effective network chain length, which is found to differ appreciably from the one expected from stoichiometry.

Introduction

The importance of the polymer–solvent interaction parameter χ in the thermodynamic behavior of polymer solutions has been established by various studies, as reviewed by Orwoll.[1] Recently, a detailed study of the thermodynamics of swollen networks was presented emphasizing the predominant role of the χ parameter.[2] A convenient experimental technique for the determination of the χ parameter is the measurement of equilibrium swelling of networks.[1]

In this study, the degree of swelling of poly(2-hydroxyethyl methacrylate) (PHEMA) networks in diethylene glycol is measured by the same experimental technique as was recently employed for the swelling of polystyrene networks.[3] The choice of the present system is motivated by both the wide range of biomedical application of PHEMA gels[4] and the possibility to proceed as a next step to ionized gels such as PHEMA–methacrylic acid copolymers in polar solvents, which are important for membrane applications. Since diethylene glycol is a good solvent for PHEMA, the influence of parameters, such as the polymer concentration during cross-linking and the cross-link density, on the equilibrium degree of swelling was clearly discernible.

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